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Synthesis of functional polymers by pre-radiation induced grafting of acrylaldehyde onto FEP film

LI Zhi WU Songliang YANG Xiangmin ZHANG Weidong YANG Cunzhong FANG Bin XIE Pengfei

Institute of Nuclear Radiation Application School of Science, East China University of Science and Technology, Shanghai 200237, China

Abstract FEP-g-acrylaldehyde graft copolymers were prepared by pre-radiation induced graft copolymerization of acryladehyde onto FEP (poly(tetrafluoroethylene-co-hexa fluoropropylene)). The effects of grafting conditions such as monomer concentration, irradiation dose, and different solvents were investigated. The formation of graft copolymers was confirmed by FT IR analysis. The structural investigation with X-ray diffraction (XRD) has been shown that the degree of crystallinity content of such graft copolymers decreases with the increment of grafting. Moreover, the content of acraldehyde onto polymer and the immobilization of protein were investigated in correlation with the degree of grafting.

Key words Pre-radiation grafting, FEP, Acryladehyde, Immobilization, Protein

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1 Introduction

Microarray technology has become a crucial tool for large-scale and high-throughput biology. It allows fast, easy and parrallel detection of thousands of addressable elements in a single experiment[1–3]. To attach proteins to a solid substate, the surface of the substate has to be modified to achieve the maximum binding capacity[4]. Aldehyde-group is one of common group for covalent binding of proteins to a surface[5], This covalent binding immobilization processes share several advantages. Usually, the active sites are better accessible to the analytes when the attachment site is positioned elsewhere. Within each antibody population, the less variation in antibody affinities upon covalent immobilization affects sensitivity positively[6,7].

Radiation-induced grafting of several monomers onto polymeric films provides a noble way to produce functional material for modern technology, especially in separation science, electrochemical devices including fuel cells, batteries and sensors in addition to biological and biomedical uses[8]. Acraldehyde has been grafted onto polyethylene and poly(methyl methacrylate) film with radiation energy[9,10], and more make to functional polymers containing hydrazone, oxime, and oxyacid[11]. However, to our knowledge, there is little detailed works about acraldehyde grafted onto FEP (poly-(tetrafluoroethylene-co-hexa fluoropropylene)) by radiation-induced graft copolymerization.

We investigated the influence of synthesis conditions on the degree of grafting using different radiation dose. FT IR-ATR and X-ray Diffraction measurements were made to prove the successful synthesis. Furthermore, the content of acraldehyde onto polymer and the immobilization of protein were investigated in correlation with the degree of grafting.

2 Experimental

2.1 Materials

FEP film of 100μm thickness supplied by Du pont (USA) was used for the grafting. Acryladehyde (from Sinopharm Chemcial Reagent Co., Ltd., China) distilled (bp 52ºC, atm. pressure) prior to use was dissolved in solvents. Other Chemicals were reagent grades and used as received.

* Corresponding author. *E-mail address*: lizhi@ecust.edu.cn
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2.2 Irradiation

FEP films were washed with methanol and dried under vacuum before irradiation. A ^{60}Co gamma ray source (10 000 Curies) was used for the irradiation of FEP films. All the irradiations were carried out in nitrogen at ambient temperature.

2.3 Graft Copolymerization

Irradiated films were cut into pieces (2.5 cm×4 cm) and were immersed in the acryladehyde solution placed in a glass ampoule. Several solvents i.e., water, ethanol, methanol, ethyl ether, and dichloromethane was used as solvent for the grafting reaction. The monomer solution was flashed with nitrogen for 30 min to remove the air, and then the ampoule was sealed. The grafting was carried out by placing the ampoule in a water bath, maintained at a constant temperature for the desired period. After the reaction, films were removed from the ampoule and extracted with ethanol to remove the homopolymer adhering to the surface of grafted films. The films were dried under vacuum at 50ºC until a constant weight was obtained. The degree of grafting was gravimeterically determined as the percentage of weight increase of the FEP film using the following equation

$$Degree\ of\ grafting/\% = \frac{w_g - w_0}{w_0} \times 100\%$$

where w_0 and w_g are the weight of original and grafted FEP films, respectively

2.4 FT IR -ATR measurements

FT IR-ATR measurements of original and grafted FEP films were carried out with an FT IR Spectrometer at ambient condition in the transmitance mode. The film spectra were detected by an ATR accessory.

2.5 X-ray diffraction measurements

X-ray diffraction (XRD) measurements were made using an X-ray diffractometer. The diffractograms were measured at 2θ, 5–50°.

2.6 Acraldehyde content

Acraldehyde content of the membranes was determined by acid-base titration. The membrane samples (about 2.0 g) were immersed into 50 mL of 0.5 M $NH_2OH{\cdot}HCl$ solution overnight at room temperature after at 45ºC with 1 h, with frequent stirring. The protons (H^+) released in the solution were titrated with standardized 0.1 M NaOH solution until yellow color turns into green. The cost of standardized NaOH solution is V_1. The same work to the 0.5 M $NH_2OH{\cdot}HCl$ solution have no membrane samples, the cost of standardized NaOH solution is V_0. The degree of acraldehyde content of the membranes determined as the following equation.

$$Acraldehyde\ Content / \% = \{[(V_1 - V_0) \times C]/m\} \times 100\%$$

where V_1 and V_0 are the cost of standardized NaOH solution of titrated $NH_2OH{\cdot}HCl$ solution have and no membranes immersed respectively. And C is the concentration of the standardized NaOH solution, and m is the weight of the membrane.

3 Results and discussion

The grafing of styren onto pre-irradiated FEP films was studied to determine optimum conditions for the preparation of membranes with desired graft levels, as show below. The grafting has been found to be strongly influenced by the reaction conditions, such as radiation dose, monomer concentration, solvent and reaction time.

3.1 Effect of radiation dose

The influence of the radiation dose on the degree of grafting is presented in Fig.1.

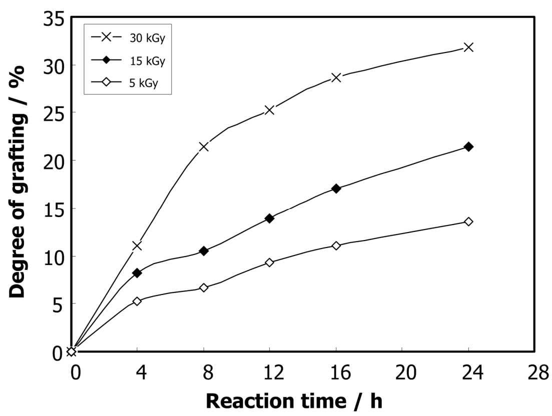

Fig.1 Variation of the degree of grafting with time at various pre-irradiation doses. Grafting conditions: monomer concentration, 100%; reaction temperature 55ºC.

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For all dose, the degree of grafting increase with the increase in irradiation dose. Such a behavior may be attributed to the fact that at higher doses of radiation, the number of radicals generated in the system also increase. Therefore, more radicals are available for grafting reaction with increasing dose.

3.2 Effect of monomer concentration

The influence of the monomer concentration on the degree of grafting is presented in Fig.2. As can be seen, the grafting degree increases with increase in monomer concentration. Moreover, the degree of grafting increases as acrylaldehyde concentration increase from 20 up to 100 vol% not too much.

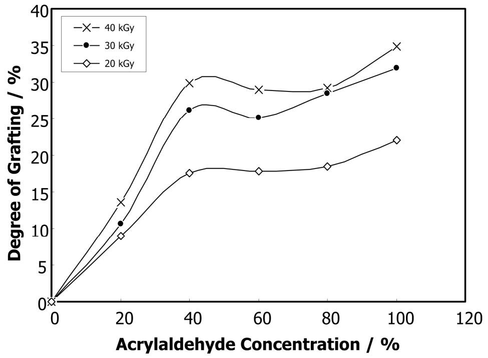

Fig.2 Grafting degree of acrylaldehyde onto FEP against monomer concentration. Grafting condition: pre-irradiation dose, 30 kGy; reaction temperature 55ºC; reaction time, 16 h.

3.3 Effect of diluent type

Diluent is basically used in radiation-induced graft copolymerization processes to bring about swelling of the base polymer, and hence enhance the degree of monomer accessibility to grafting sites. Therefore, the correct choice of diluent is one of the radiation-induced grafting techniques.

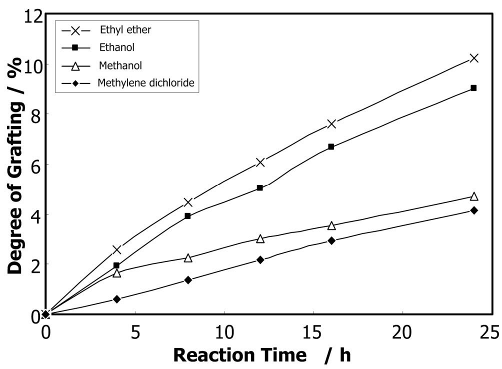

Fig.3 Grafting degree of acrylaldehyde onto FEP against reaction time at different diluent.

3.4 FT IR Measurements

Figure 4 shows FTIR spectra of the original and grafted FEP films. The original FEP films are characterized by narrow band at 1100–1200 cm^{-1}, which represents the stretching vibration of C-F. The presence of an aldehyde of acryladehyde in grafted FEP films is established by the C=O stretching vibration at 1710 cm^{-1} and the C-H of aldehyde stretching vibrations at 2850 cm^{-1}. The spectra clearly indicate that the bands arising from the presence of aldehyde increase with the increase in the degree of grafting. This means that acryladehyed is successfully grafted to the FEP backone.

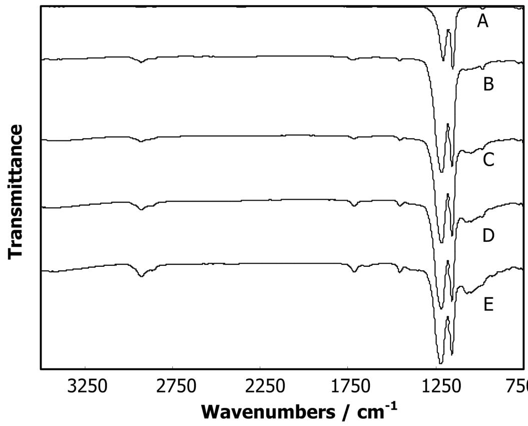

Fig.4 FT IR-spectra of original FEP (A) and acraldehyde-grafted FEP membranes having various degrees of grafting: (B) 5.21%, (C) 10.52%, (D) 17.05%, (E) 28.65%.

3.5 X-ray diffraction measurements

The grafting of acryladehyde onto FEP has been found to bring about considerable changes in the crystallinity of the graft copolymer. Fig.5 shows the diffraction patterns of the original and grafted FEP films.

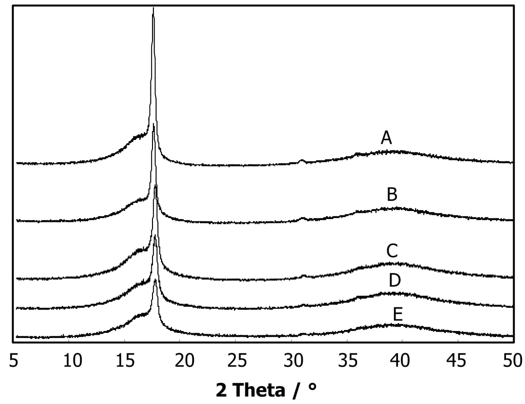

Fig.5 Diffraction patterns of original FEP (A) and acraldehyde-grafted FEP membranes having various degrees of grafting: (B) 5.21%, (C) 10.52%, (D) 17.05%, (E) 28.65%.

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It was found that the crystallinity peak for the original and all grafted films occurs at the same angle (2θ), meaning that there is no change in the structure. However, the peak intensities of all grafted films are lower, and decrease with the increase in the degree of grating. This means that the crystallinity decrease with the increase in the degree of grafting. It can be noticed that these results are similar to those obtained upon grating of styrene onto FEP, styrene onto PFA. This behavior can be explained on the bases of dilution and partial destruction of the inherent crystallinity.

3.6 Acraldehyde content

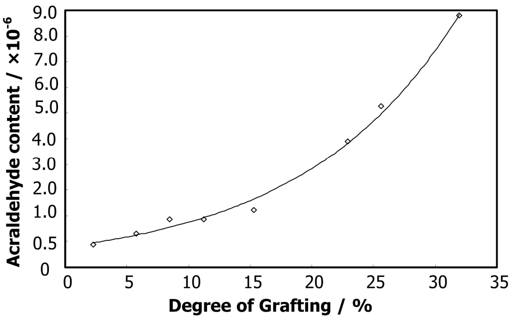

Fig.6 Relationship between acraldehyde content of the grafted membrane and the degree of grafting.

4 Conclusion

FEP-g-acrylaldehyde graft copolymers were prepared by pre-radiation induced graft copolymerization of acryladehyde onto FEP (poly(tetrafluoroethylene-co-hexa fluoropropylene)). The effects of grafting conditions such as monomer concentration, irradiation dose, and various solvents were investigated. The formation of graft copolymers was confirmed by FTIR analysis. The structural investigation by X-ray diffraction (XRD) revealed that the degree of crystallinity content of such graft copolymers decrease with the increase in grafting. Moreover, the content of acraldehyde onto polymer and the immobilization of protein were investigated in correlation with the degree of grafting.

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